PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C25B 15/08, 1/16

A1

(11) International Publication Number: WO 99/07919

(43) International Publication Date: 18 February 1999 (18.02.99)

(21) International Application Number: PCT/GB98/02395

(22) International Filing Date: 10 August 1998 (10.08.98)

(30) Priority Data:
97/7095 8 August 1997 (08.08.97) ZA

(71) Applicant *(for all designated States except US)*: INCHEM (PROPRIETARY) LIMITED [ZA/ZA]; 6 Burry Koen Road, Jetpark, Boksburg 1459 (ZA).

(71) Applicant *(for IS only)*: SKONE JAMES, Robert, Edmund [GB/GB]; Gill Jennings & Every, Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).

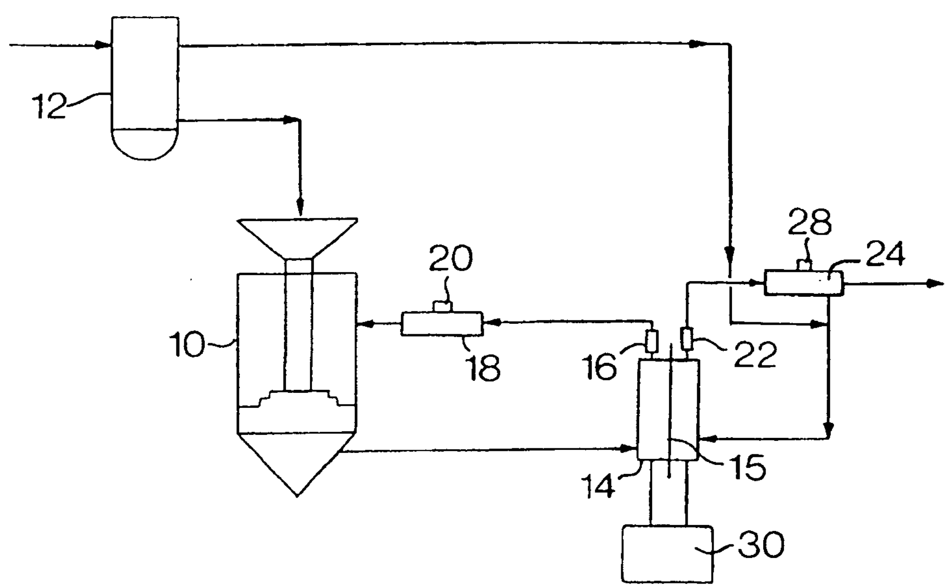
(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: GOSS, Desmond, Brian [ZA/ZA]; 10 Fairbridge Street, Farrarmere, Benoni 1601 (ZA). GOSS, Bowen, Clyde [ZA/ZA]; 3 The Grange, Cowley Road, Bryanston 2021 (ZA). ROSELAAR, Hendrik, Albert [ZA/ZA]; 5 Ashton Way, Lonehill Upper East, Sandton 2196 (ZA).

(74) Agent: GILL JENNINGS & EVERY; Broadgate House, 7 Eldon Street, London EC2M 7LH (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: METHOD AND APPARATUS FOR GENERATING A GAS



(57) Abstract

A method of generating a gas commences by forming a solution in a reservoir. The solution is then fed through an electrolysis cell so as to liberate the gas from the solution. The mixture of the solution and gas discharged from the cell is heated by passing it through a heating tube. This causes it to self-circulate back to the reservoir by means of a thermosyphon effect. Finally, the liberated gas and the solution are passed through a gas separator to separate the gas from the solution prior to circulating the solution back to the reservoir. The gas generated by the method of the invention is typically a halogen, and in particular, chlorine, produced by the electrolysis of a brine solution. The apparatus of the invention is arranged for producing chlorine gas in accordance with the above method in a safe and effective manner without the need of costly circulation pumps.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

METHOD AND APPARATUS FOR GENERATING A GAS

BACKGROUND OF THE INVENTION

THIS invention relates to a method and an apparatus for generating a gas. In particular the invention relates to a method and an apparatus for generating chlorine gas.

Devices for generating chlorine gas are known. Some of the known devices generate chlorine by passing sodium chloride and water through an electrolysis cell. As the solution passes through the cell, chlorine gas is liberated from the solution on the anolyte side of the cell, while hydrogen gas and caustic soda are generated on the catholyte side of the cell.

Generally, such devices require pumps to circulate the anolyte and catholyte solutions respectively in the device. The presence of the pumps increases the capital and operating costs of the device and contributes to the possibility of breakdowns.

SUMMARY OF THE INVENTION

According to the first aspect of the invention there is provided a method of generating a gas comprising the steps of:

forming a solution in a reservoir;

feeding the solution through an electrolysis cell so as to liberate a gas from the solution;

heating the mixture of the solution and gas discharged from the cell causing it to circulate back to the reservoir by means of a thermosyphon effect; and

passing the liberated gas and the solution through a gas separator to separate the gas from the solution prior to circulating the solution back to the reservoir.

The solution is preferably strengthened in the reservoir before being returned to the cell.

The gas generated by the method of the invention may be a halogen, and in particular, chlorine.

In the preferred form of the invention, the step of liberating a gas from the solution includes the step of generating chlorine gas and depleted brine solution on an anolyte side of the electrolysis cell and hydrogen and caustic soda on a catholyte side of the electrolysis cell when a brine solution of water and sodium chloride is fed into the cell. In this regard, the step of forming a solution in a

reservoir may comprise feeding sodium chloride and water into a brine resaturater to produce a brine solution.

Preferably, the caustic soda and the hydrogen are passed through a hydrogen separator to separate the hydrogen from the caustic soda.

At least some of the caustic soda may be recirculated through the electrolysis cell. For this purpose, water may be added to the caustic soda to maintain the desired concentration and to compensate for discharge of concentrated caustic soda from the system.

Conveniently, at least some of the caustic soda and the chlorine generated from the method of the invention are reacted to produce sodium hypochlorite.

The heating of the mixture of the solution and gas may be effected by passing the mixture through a heating tube.

The method of the invention may further include the step of sensing the liquid level in the reservoir and feeding additional water into the reservoir when the liquid level falls below a predetermined level.

Conveniently, water is passed through a purification unit prior to being fed into the reservoir.

According to a second aspect of the invention there is provided an apparatus for generating a gas comprising:

a reservoir for containing a solution;

an electrolysis cell in fluid communication with the reservoir for liberating a gas from the solution when the solution is passed therethrough;

means for heating the mixture of the solution and gas discharged from the cell causing it to circulate back to the reservoir by means of a thermosyphon effect; and

a gas separator in fluid communication with the electrolysis cell and the reservoir for separating the liberated gas from the solution prior to circulating the solution back to the reservoir.

The gas generated by the apparatus of the invention may be a halogen. Preferably, the halogen is chlorine.

Conveniently, the reservoir is in the form of a brine resaturator for forming a brine solution from water and sodium chloride.

Preferably, flow through the brine resaturator is in a downward direction.

The gas separator may be a chlorine separator in fluid communication with an anolyte side of the electrolysis cell for separating liberated chlorine gas from a depleted brine solution of water and sodium chloride.

Preferably, the device also includes an additional gas separator in fluid communication with a catholyte side of the electrolysis cell for separating liberated hydrogen from caustic soda, generated on the catholyte side of the cell.

The caustic soda outlet of the hydrogen separator may be in fluid communication with the catholyte side of the electrolysis cell to allow the caustic soda to be recirculated through the electrolysis cell.

The apparatus of the invention may include means for flushing the apparatus when the level of impurities in the brine solution rises above a predetermined level.

Conveniently, the device includes a water purification unit for purifying water prior to feeding the water into the brine resaturator.

BRIEF DESCRIPTION OF THE ACCOMPANYING DRAWINGS

Figure 1 shows a flow chart of the method of the invention;

Figure 2 shows, diagrammatically, a plan view of the gas generating apparatus of the invention;

Figure 3 shows, diagrammatically, a side view of the apparatus illustrated in Figure 2;

Figure 4 shows, diagrammatically, a front view of the apparatus illustrated in Figure 2;

Figure 5 shows a plan view, in partial cross-section, of one of the electrolysis cells of the apparatus illustrated in Figure 2;

Figure 6 shows a cross-sectional view of the electrolysis cell illustrated in Figure 5 along the line 6-6; and

Figure 7 shows a cross-sectional view of the electrolysis cell illustrated in Figure 6 along the line 7-7.

DETAILED DESCRIPTION OF THE INVENTION

Figure 1 of the drawings shows a flow chart of one embodiment of the method of the invention. In this embodiment of the invention, a brine solution of sodium chloride and water is depleted in the production of chlorine gas, hydrogen gas, and caustic soda.

With reference to Figure 1, water is fed into a reservoir in the form of a brine resaturator 10 via a water purification unit 12. The brine resaturator 10 has a salt bed (not shown) for receiving sodium chloride, and the purified water discharged from the water purification unit 12 is introduced into the brine resaturator.

As the sodium chloride is dissolved in the water, a brine solution is formed in the brine resaturator. The brine solution flows from the brine resaturator to an electrolysis cell 14 where it enters the anolyte side of the electrolysis cell (the left hand side of the cell in Figure 1). As the brine solution passes through the electrolysis cell 14, chlorine gas is liberated from the solution on the anolyte side of the cell, while hydrogen gas is liberated and caustic soda generated on the catholyte side of the cell by sodium ions passing through an ion exchange membrane 15.

The electrolysis cell 14 includes a plurality of baffles (not shown) which support the electrodes.

The liberated chlorine gas and the depleted brine solution discharged from the anolyte side of the electrolysis cell are directed through a heating tube 16 which increases the temperature of the fluid, thereby assisting the flow of the fluid by means of convection.

Thereafter the chlorine gas and depleted brine solution are passed through a chlorine separator 18 for separating the chlorine gas from the brine solution. The chlorine separator 18 includes an outlet 20 for discharging the chlorine gas. The chlorine gas discharged from the separator 18 is then discharged externally for consumption, while the depleted brine solution is recirculated back to the brine resaturator 10 for resaturation.

The lower density of the brine/chlorine gas mixture and the convection caused by the increase in the fluid temperature together cause the fluids to circulate through the electrolysis cell and the chlorine separator, whilst depleted brine circulates downwards through the brine resaturator.

On the catholyte side of the electrolysis cell (right hand side of the cell in Figure 1), the hydrogen gas and caustic soda are also discharged from the electrolysis cell, and pass through a heating tube 22 prior to entering a hydrogen separator 24.

The hydrogen gas is discharged from the hydrogen separator 24 through a gas outlet 28 and the caustic soda solution is recirculated through the electrolysis cell 14, as shown.

Purified water is continuously added to the caustic soda solution recirculating through the electrolysis cell in order to regulate the concentration of this

solution and the displaced caustic soda solution is directed into a storage vessel (not shown).

Similarly to the flow of fluids through the anolyte side of the electrolysis cell, the flow of the fluid through the catholyte side of the electrolysis cell is achieved by a thermosyphon action.

A reticfier 30 provides the electrolysis cell 14 with direct current. Since the production rate of the chlorine is directly proportional to the supply current, the current is regulated to provide for a consistent rate of chlorine production.

Changes in the surface level of the liquid in the brine resaturator are sensed by a level sensor (not shown) which is electronically connected to the water feed. In this way, as the surface of the liquid in the brine resaturator falls below a predetermined level, additional water is automatically introduced into the brine resaturator. Salt is fed into the brine resaturator periodically to maintain a substantially constant concentration of brine solution within the brine resaturator 10.

With reference now to Figures 2 to 7 of the drawings, a brine solution formed in a brine resaturator 36 is directed to the anolyte sides 49 of the electrolysis cells 38 and 40 through a conduit 42, as shown, and enters the electrolysis cells at lower regions thereof through inlet apertures 44.

With particular reference to Figures 5 to 7, an anolyte side of each electrolysis cell includes four baffles 46 which support the anode relative to the membrane 15.

The anolyte side 49 and the catholyte side 50 of each electrolysis cell are attached to one another by means of a series of bolts 52 which pass through a plurality of apertures 53 spaced around the periphery of the anolyte and the catholyte sides of the electrolysis cell. An ion exchange membrane 54 is sandwiched between the anolyte and the catholyte sides of the cell, as shown most clearly in Figure 5.

Referring back to Figures 2 to 4, heating tubes 57 are connected to the outlet of the anolyte and the catholyte sides of each electrolysis cell, as illustrated. The heating tubes 57 increase the temperature of the fluids flowing therethrough and consequently assist in the flow of the fluids by means of convection, as mentioned above.

The fluids exiting the anolyte side 49 of the cells 38 and 40 are directed through the heating tube 57 as they are conveyed to a chlorine separator 58 along a conduit 60. The chlorine gas is discharged from the chlorine separator by means of an outlet 20 to be consumed externally, while the depleted brine solution is returned to the brine resaturator 36 for resaturation.

Similarly, caustic soda and hydrogen leaving the catholyte side 50 of the cells 38 and 40 are directed to a hydrogen separator 64 via flexible tubes 56 and heater tube 57 through conduit 66, where the hydrogen is separated from the caustic soda. Hydrogen is vented to atmosphere via outlet 28, while a displaced portion of the caustic soda is fed into a storage tank 66 and the remaining portion of the caustic soda is recirculated through the electrolysis cells 38 and 40 via a conduit 70.

The electrolysis cells are powered by a direct current electrical power source (not shown), as mentioned above. In order to maintain a low consumption of

electricity, it is important to ensure that "blinding" of the membranes does not occur, and therefore that the brine and caustic soda that contact the membranes are relatively free of undesirable impurities. It is for this reason that purified water and salt are used to form the brine solution, and purified water is added to the caustic soda, when required.

During tests on a prototype of the invention, a power consumption of 3.5 AC kWh per kilogram of chlorine was achieved. In the prototype, the anodes were Dimensionally Stable Anodes available from DeNora, the cathodes were stainless steel cathodes also available from DeNora, and the membranes were Nafion 324 membranes produced by DuPont.

To ensure that the unit shuts down safely and that no damage occurs, especially to the cells and the ion exchange membranes, an automatic sequence is activated on shut-down that purges the chlorinated brine from the anolyte circuit using fresh, purified water prior to the water and power supply being automatically turned off.

Furthermore, in order to prevent the cells from running dry and short circuiting, high temperature trips are installed on both the caustic soda and the brine solution outlets from the cells. In the event that the circulation rate of either of these circuits decreases substantially, the power supply is automatically turned off. Similarly, if the voltage across the cells exceeds a preset limit, the power supply is automatically turned off. The apparatus also includes a chlorine leak detector for automatically shutting down the apparatus in the event of a chlorine leak.

The apparatus of the embodiment of the invention described above is relatively compact and can be used in a variety of locations. In this regard, the apparatus

can even be used in rural areas to provide chlorine for water purification on a relatively small scale in a safe and effective manner. In such a case a generator may be used to provide electrical power for the apparatus. In addition, sodium hypochlorite, which can be used as a bleaching agent, water disinfectant, fungicide, or laundering reagent, for example, can be produced by the same apparatus.

CLAIMS

1. A method of generating a gas comprising the steps of:

   forming a solution in a reservoir;

   feeding the solution through an electrolysis cell so as to liberate a gas from the solution;

   heating the mixture of the solution and gas discharged from the cell causing it to circulate back to the reservoir by means of a thermosyphon effect; and

   passing the liberated gas and the solution through a gas separator to separate the gas from the solution prior to circulating the solution back to the reservoir.

2. A method according to claim 1, wherein the solution is strengthened in the reservoir before being returned to the cell.

3. A method according to claim 1 or claim 2, wherein the gas generated by the method is a halogen.

4. A method according to claim 3, wherein the halogen is chlorine.

5. A method according to any one of the preceding claims, wherein the step of liberating a gas from the solution includes the step of generating chlorine gas and depleted brine solution on an anolyte side of the electrolysis cell and hydrogen and caustic soda on a catholyte side of the

electrolysis cell when a brine solution of water and sodium chloride is fed into the cell.

6. A method according to claim 5, wherein the step of forming a solution in a reservoir comprises feeding sodium chloride and water into a brine resaturator to produce a brine solution.

7. A method according to claim 5 or claim 6, wherein the caustic soda and the hydrogen are passed through a hydrogen separator to separate the hydrogen from the caustic soda.

8. A method according to claim 7, wherein at least a portion of the caustic soda is recirculated through the electrolysis cell.

9. A method according to claim 8, wherein water is added to the caustic soda to maintain the desired concentration and to compensate for discharge of concentrated caustic soda from the system.

10. A method according to claim 7, wherein at least a portion of the caustic soda and the chlorine generated from the method of the invention are reacted to produce sodium hypochlorite.

11. A method according to any one of the preceding claims, wherein the mixture of the solution and gas is heated by passing the mixture through a heating tube.

12. A method according to any one of the preceding claims, including the step of sensing the liquid level in the reservoir and feeding additional

water into the reservoir when the liquid level falls below a predetermined level.

13. A method according to claim 12, wherein the water is passed through a purification unit prior to being fed into the reservoir.

14. An apparatus for generating a gas comprising:

a reservoir for containing a solution;

an electrolysis cell in fluid communication with the reservoir for liberating a gas from the solution when the solution is passed therethrough;

means for heating the mixture of the solution and gas discharged from the cell causing it to circulate back to the reservoir by means of a thermosyphon effect; and

a gas separator in fluid communication with the electrolysis cell and the reservoir for separating the liberated gas from the solution prior to circulating the solution back to the reservoir.

15. An apparatus according to claim 14, wherein the gas generated by the apparatus is a halogen.

16. An apparatus according to claim 15, wherein the halogen is chlorine.

17. An apparatus according to any one of claims 14 to 16, wherein the reservoir is in the form of a brine resaturator for forming a brine solution from water and sodium chloride.

18. An apparatus according to any one of claims 14 to 17, wherein the gas separator is a chlorine separator in fluid communication with an anolyte side of the electrolysis cell for separating liberated chlorine gas from a depleted brine solution of water and sodium chloride.

19. An apparatus according to any one of claims 14 to 18, including a hydrogen gas separator in fluid communication with a catholyte side of the electrolysis cell for separating liberated hydrogen from caustic soda, generated on the catholyte side of the cell.

20. An apparatus according to claim 19, wherein a caustic soda outlet of the hydrogen separator is in fluid communication with the catholyte side of the electrolysis cell to allow the caustic soda to be recirculated through the electrolysis cell.

21. An apparatus according to any one of claims 14 to 20, including means for flushing the apparatus when the level of impurities in the brine solution rises above a predetermined level.

22. An apparatus according to claim 21, including a water purification unit for purifying water prior to feeding the water into the brine resaturator.

23. A method according to claim 1 substantially as herein described with reference to the accompanying drawings.

24. An apparatus according to claim 14 substantially as herein described with reference to the accompanying drawings.

FIG 1

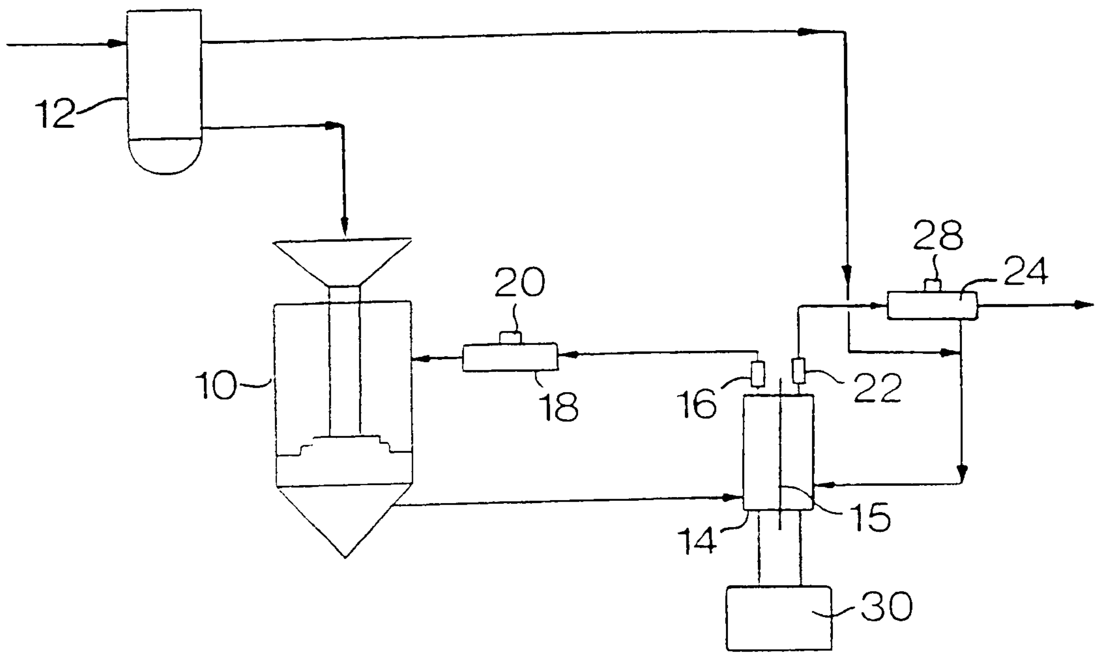


FIG 6

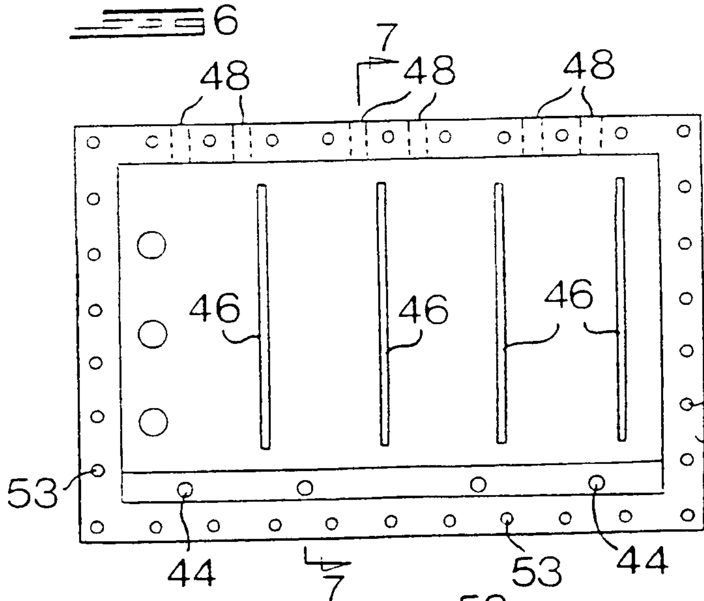
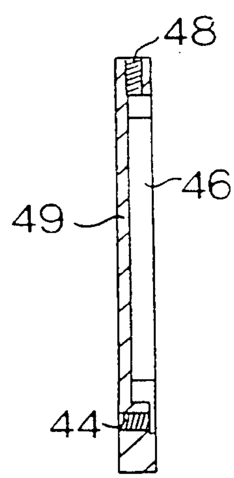


FIG 7



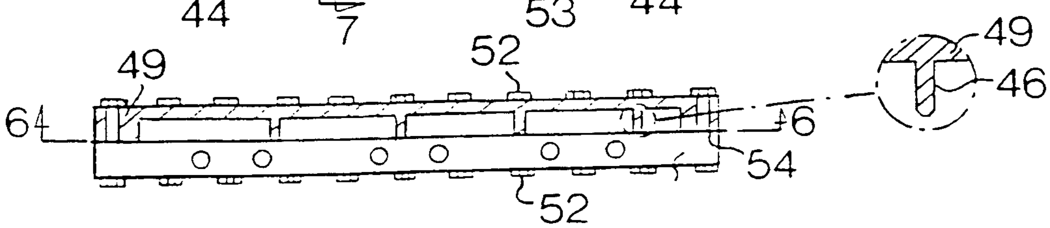


FIG 5

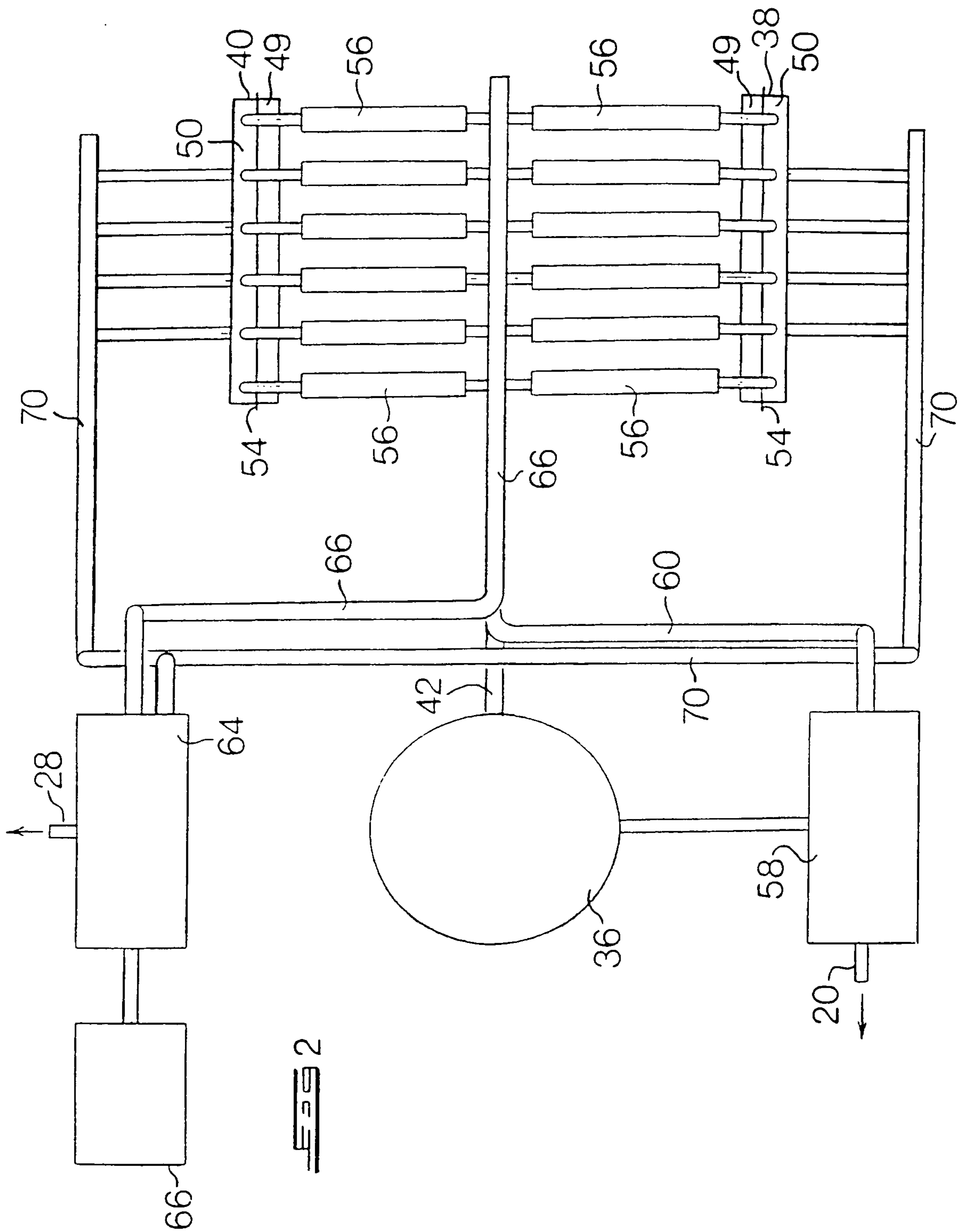

40
49
56
56
49
38
50
50
70
70
54
56
56
54
66
66
60
70
42
64
28
58
36
20
66

FIG 2

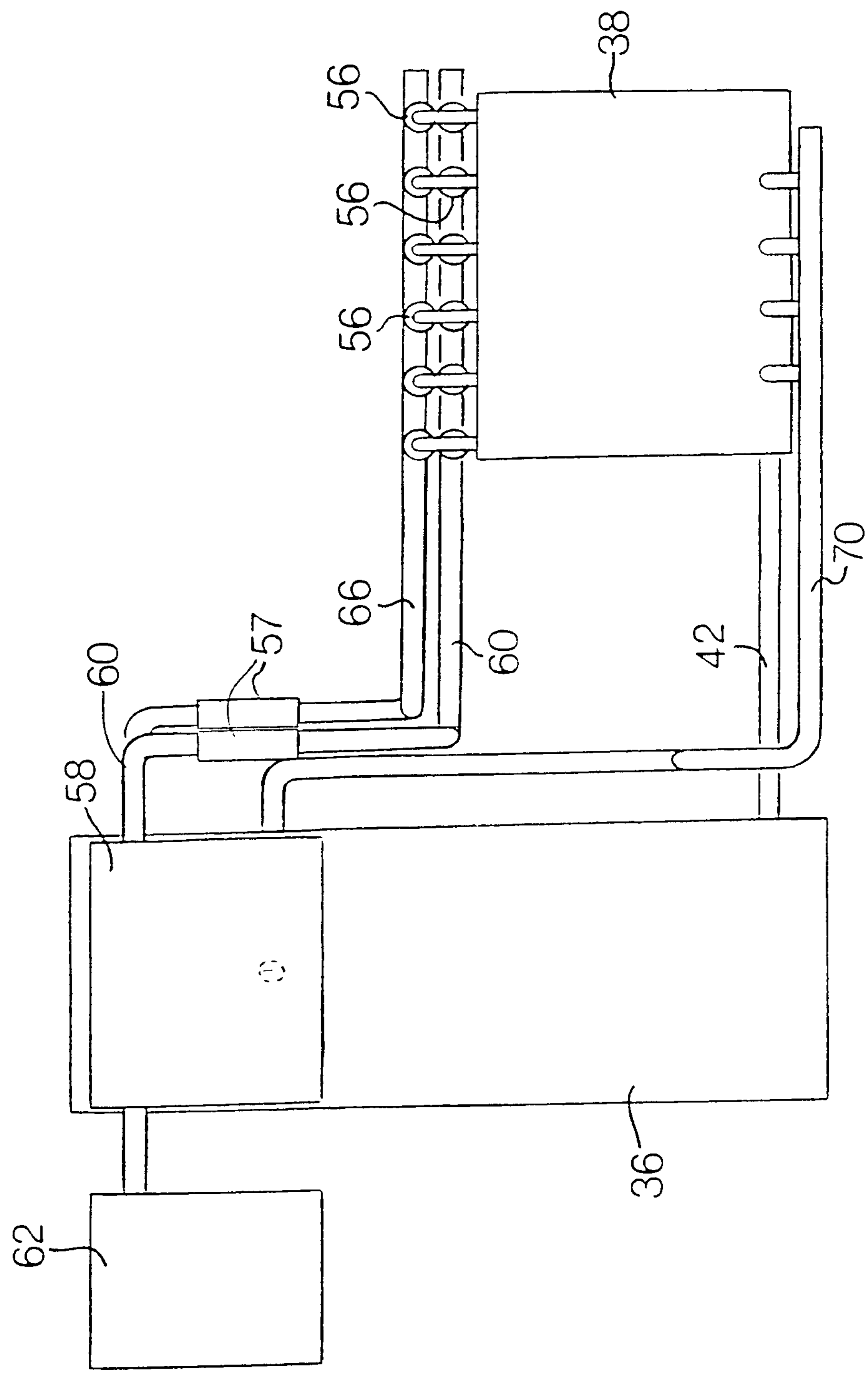


FIG. 3

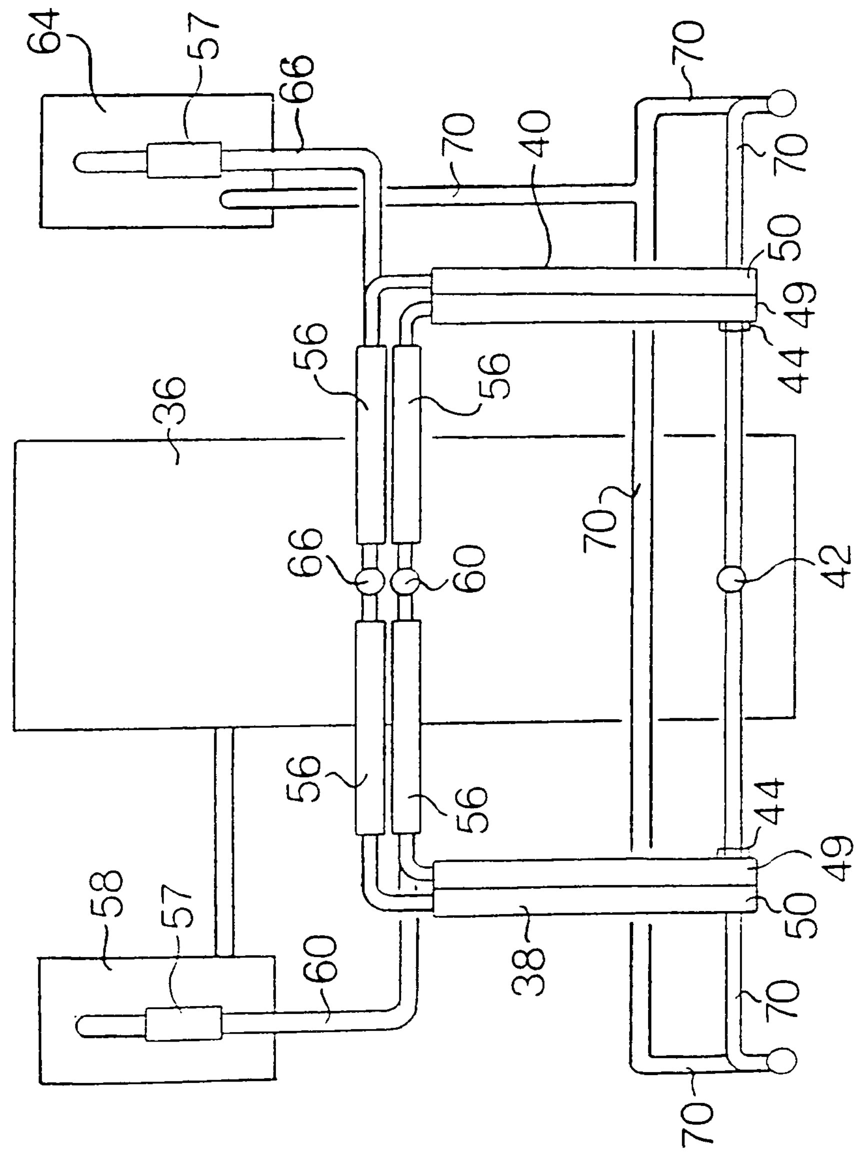


Fig. 4

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/GB 98/02395

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C25B15/08 C25B1/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C25B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	EP 0 419 052 A (NEIL SUSAN ANN) 27 March 1991 see claim 1	1
A	US 4 059 495 A (DE NORA ORONZIO ET AL) 22 November 1977 see claim 1	1
A	US 4 198 277 A (FITCH ROBERT H ET AL) 15 April 1980	1
A	FR 2 410 058 A (ELECTRICITE DE FRANCE) 22 June 1979 see claim 3	1
A	US 4 256 814 A (AVIGAL YITZHAK ET AL) 17 March 1981 see claim 1	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 November 1998	07/12/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Clement, J-P

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/GB 98/02395

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0419052 A	27-03-1991	AU 6124490 A	28-02-1991
US 4059495 A	22-11-1977	NONE	
US 4198277 A	15-04-1980	EP 0002783 A	11-07-1979
		JP 1364363 C	09-02-1987
		JP 54096498 A	30-07-1979
		JP 61028753 B	02-07-1986
FR 2410058 A	22-06-1979	NONE	
US 4256814 A	17-03-1981	NONE	

Form PCT/ISA/210 (patent family annex) (July 1992)